



Collision Widths of CO Lines Broadened by Water Vapor at Elevated Temperatures

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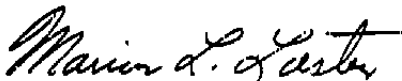
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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) The collisional or Lorentz broadening by water vapor of the P(2), P(3), and P(7) absorption lines of the fundamental band of CO was studied at seven temperatures ranging from 400 to 1000 K. The Lorentz half width was determined by a parametric fit of the measured line shape to the Voigt profile. The half width at standard temperature was found by fitting the data for each line to $\gamma(T) = \gamma(T_0)(T/T_0)^{-N}$. The value of N for the P(2) line was found to be -0.73433 ± 0.00674 , for the P(3) line -0.70168 ± 0.00073 , and for the P(7) line -0.76686 ± 0.00006 .		

PREFACE

The work reported herein was conducted by the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), Arnold Air Force Station, TN 37389. The results were obtained by Sverdrup Technology, Inc., AEDC Group, operating contractor for the propulsion test facility at AEDC under Sverdrup Project No. E32M-C31. The Air Force Program Manager was Lt. S. W. Lehr. The Sverdrup Project Manager was H. C. Walker, Jr. The manuscript was submitted for publication on July 5, 1983.

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1.0 INTRODUCTION

A non-intrusive method of measuring concentration and temperature of specific molecules in the exhaust stream of rocket and turbine engines is being sought to replace the probe methods currently being used. The probe methods being used provide results which are subject to question as the probe itself may chemically alter the exhaust gas composition. The tunable diode laser (TDL) spectrometer system is being developed as a possible replacement for the probes.

The TDL measurements can be made by passing the laser beam through the exhaust gases as they exit the engine. The energy absorbed from the laser beam is related to species concentration; i.e., the absorption is proportional to the number of absorbing molecules in the beam. The absorption also depends on wavenumber (line shape), as well as a line strength function which is temperature dependent. The line shape is affected by collisions with the absorbing molecules; therefore, the absorption is a function of the partial pressure of each gas present. Each gas present has a characteristic effect on the shape of the absorption line. In order to make accurate measurements, the instrument should be capable of recording true line shapes.

The TDL, which has a line width on the order of 10^{-4} wavenumber, provides, for all practical purposes, the true line shape since many absorption lines have a full width at half maximum (FWHM) of 0.1 to 0.2 wavenumbers. Additionally with the TDL, the exhaust gas temperature can be determined by the two-line technique which makes use of the temperature dependence of the line strength function.

The TDL spectroscopy system has been used in the laboratory to make a detailed study of representative lines in the CO fundamental band at 4.7μ which can be used for concentration and temperature determinations. In the past this method has been calibrated for CO broadened by nitrogen and carbon dioxide. In the present report this method is calibrated for CO broadened by water vapor.

The half width of three CO absorption lines broadened by water vapor was studied as a function of temperature with a tunable diode infrared laser. Measurements were made on the P(2), P(3), and P(7) lines at temperatures ranging from 400 to 1000 K with the purpose of determining the variation with temperature and rotational quantum number of the water vapor broadening of CO lines. The results, which were taken at various pressures, were extrapolated to standard temperature and pressure. A full discussion of the pertinent theory is found in Refs. 1 and 2; therefore, only a condensed description follows.

2.0 THEORY

The intensity of radiation that has passed through an optical path length ℓ of a homogeneous layer of sample gas is given by the Lambert-Beers Law:

$$I(\omega) = I_0(\omega)e^{-k(\omega)\ell} \quad (1)$$

where $I_0(\omega)$ is the radiation intensity incident on the sample, $I(\omega)$ is the intensity transmitted by the sample, and the absorption coefficient, $k(\omega)$, is a parameterized function of the wavenumber ω . For an isolated absorption line, the absorption coefficient may be written

$$k(\omega) = S\phi(\omega - \omega_0)P \quad (2)$$

where $S(\text{cm}^{-2} - \text{atm}^{-1})$ is the integrated intensity of the line normalized to atmospheric pressure, $p(\text{atm})$ is the partial pressure of the absorbing gas, and $\phi(\omega - \omega_0)$ is the normalized line-shape function.

Under conditions for which both Doppler and pressure broadening are important, the line-shape function, $\phi(\omega - \omega_0)$, is given by the Voigt profile:

$$\phi(\omega - \omega_0) = \frac{(\ln 2/\pi)^{1/2}}{\gamma_D \pi} a \int_{-\infty}^{\infty} \frac{e^{-y^2} dy}{a^2 + (x - y)^2} \quad (3)$$

where γ_D is the Doppler half width, a is the Voigt parameter

$$a = \frac{(\ln 2)^{1/2} \gamma_L}{\gamma_D}$$

γ_L is the pressure-broadened or Lorentzian half width, and

$$x = \frac{2(\ln 2)^{1/2} (\omega - \omega_0)}{\gamma_D}$$

is proportional to the distance from the line center. The experimental line shape is fitted to the Voigt profile by a nonlinear least-squares procedure for which the line strength and Lorentz half width are adjustable parameters. Since γ_L varies linearly with pressure, measurements made at different pressures can be used to determine γ_L^0 , the Lorentzian half width at atmospheric pressure.

Data taken at different temperatures can be used to compute the half width at a standard temperature by fitting the γ_L to

$$\gamma_L(T) = \gamma_L^0(T_0)(T/T_0)^{-N} \quad (4)$$

a relationship determined by Birnbaum (Ref. 3) that has been used successfully by others (Refs. 1 and 3 through 7) for the temperature dependence of CO half widths.

3.0 EXPERIMENT

The spectra were taken with a Laser Analytics tunable diode laser spectrometer. Details of the system are described in Ref. 2. Optics external to the spectrometer allowed measurements to be made through the heated sample cell located in a three-element, 2000-w furnace. Figure 1 is a schematic of the optical system. The sample cell consisted of sapphire windows bonded to Kovar® flanges, which were welded to a 3-in.-long stainless-steel pipe. The temperature was monitored by a thermocouple inside the cell. The detector was a liquid-nitrogen-cooled indium antimonide infrared detector with peak wavelength response near 5 μ .

After the sample cell, the beam passed through a calibration cell that could be filled with CO to a pressure sufficient to saturate the absorption line. The signal level at the saturation provided the spectral zero intensity level for analysis of the absorption spectra. A 3-in. germanium etalon mounted on a slide could be introduced into the beam. At 2115 cm^{-1} the etalon produced fringes with a spacing of 0.0163 cm^{-1} which were used to monitor the tuning of the laser.

For each spectrum recorded, CO was admitted into the evacuated sample cell after the laser had been tuned to the center of an absorption line. The cell pressure was then reduced until the line was no longer saturated. Water vapor was obtained by heating liquid water to the temperature that corresponded to the desired vapor pressure. The vapor was supplied to the sample cell through previously evacuated heated transfer lines and valves which were maintained at 400 K to prevent recondensation. The pressure was also monitored by means of a heated pressure transducer.

The data acquisition system consisted of an analog signal processor, a minicomputer, and a digital tape drive to record the data on 7-track tape. Following each data point taken at known pressure and temperature, the cell was pumped out and a 100-percent transmission scan recorded. Figure 2 shows an example of raw data, including the 100-percent transmission and etalon traces. The residual CO absorption, used to check laser stability, was removed from the trace before analyzing the data.

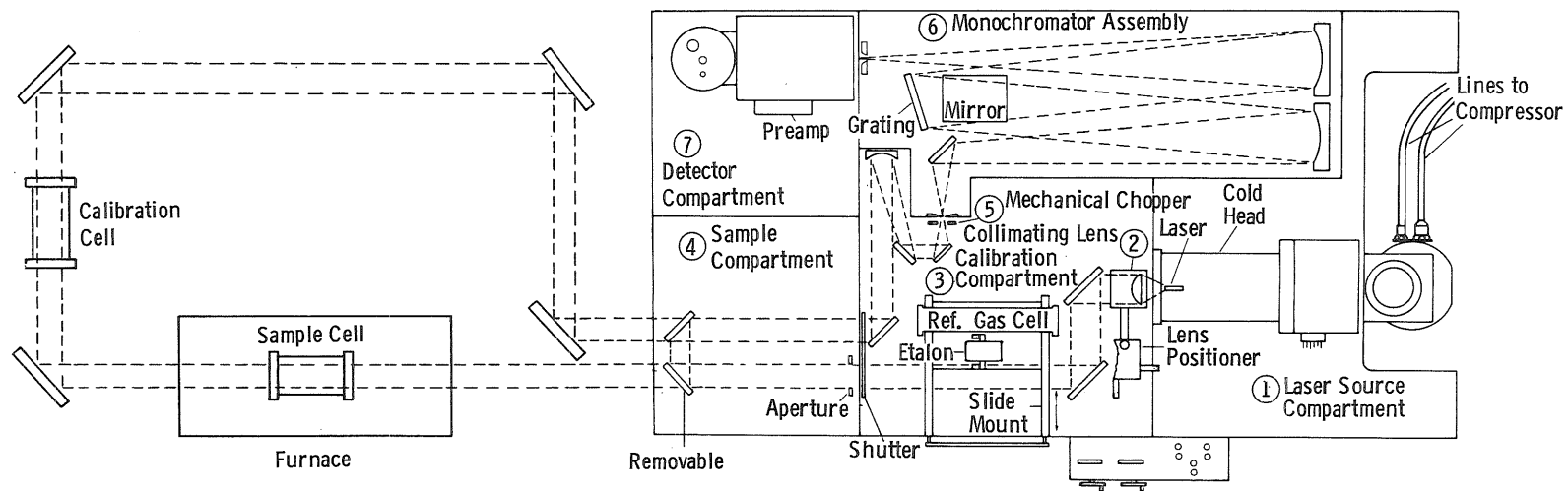


Figure 1. Laboratory optical system.

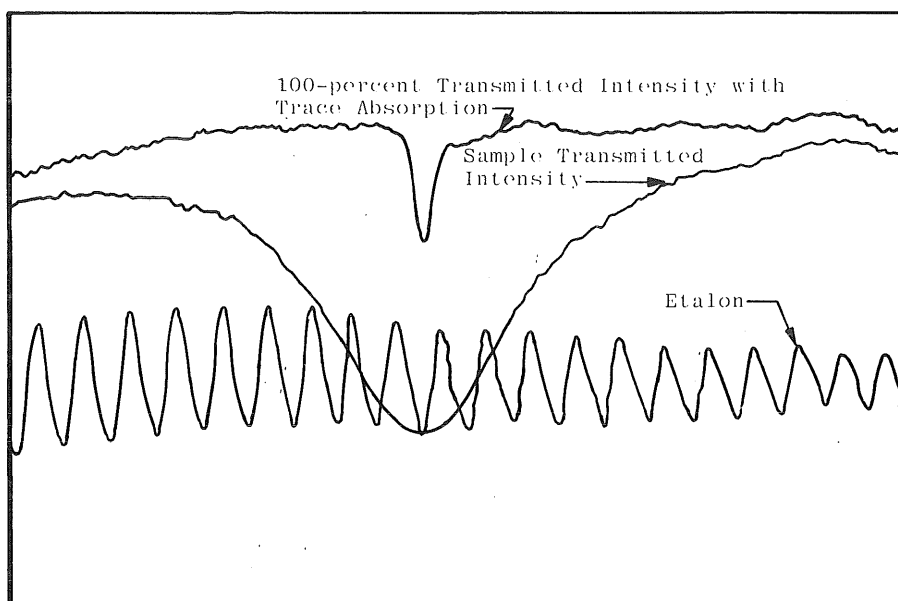


Figure 2. Typical data point showing the various transmission measurements needed to evaluate each data point.

The amount of radiation absorbed by the gas sample is the difference between the amount of radiation transmitted to the detector with and without the gas sample present in the beam path. First, the 100-percent transmission trace was smoothed using a least-squares procedure; then, the absorption line was fitted to a Voigt profile by a least-squares procedure that used as many as 75 iterations. The line strength and Lorentzian half widths were the adjustable parameters whose values were determined by the fit. Figure 3 shows the same data point after analysis.

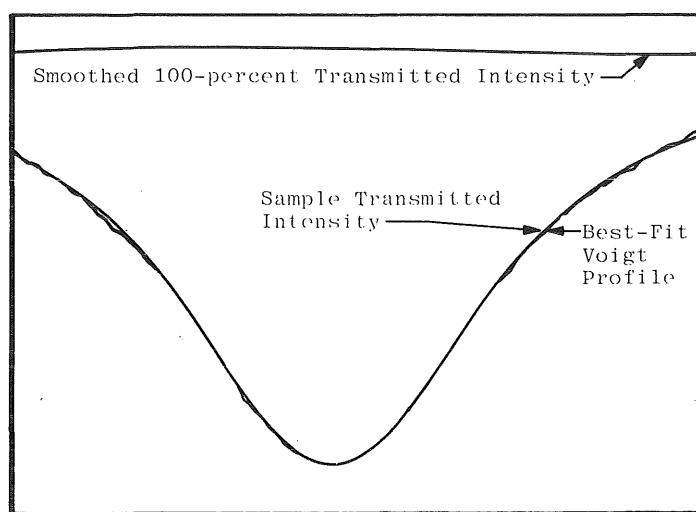


Figure 3. Data point after analysis.

4.0 RESULTS

Data were taken on the P(2), P(3), and P(7) absorption lines of the fundamental band of CO at temperature intervals of 100 K from 400 to 1000 K. Six to ten data points were taken at each temperature with the water vapor pressure in the range from 5 to 7 psia, depending on the temperature of the water bath. Since the half width is assumed to vary linearly with pressure, each half width determined by the fit to the Voigt profile could be adjusted to give the half width at atmospheric pressure. All the data were taken at temperatures within a few degrees of a multiple of 100 K. The half widths determined from the Voigt profile were then fitted to Eq. (4) in order to determine the value of N. Equation (4) and the determined value of N were then used to adjust the data a few degrees to an even multiple of 100 K. An error analysis was conducted on the data, and the probable error, shown in Tables 1 and 2, was calculated for each data point.

The absorption line half widths normalized to atmospheric pressure and extrapolated to room temperature are shown in Table 1 for the three CO lines studied. Also shown are the values of N from Eq. (4) used in the extrapolation, the standard deviation of N, and the total number of data points taken. In Table 2 the average values of the line half widths at the temperatures studied are presented normalized to atmospheric pressure. In Figs. 4, 5, and 6, the half-width data are plotted as a function of temperature; also shown are the data previously obtained by Lowry and Fisher (Ref. 8) using a copper absorption cell rather than the stainless-steel cell used here. For comparison to the extrapolated results of this work, the room temperature data of Varghese and Hanson (Ref. 9) are also shown. These are the only known published values of CO broadened by water vapor, and the extrapolated room temperature values reported here are about 15-percent lower than the Varghese and Hanson values. However, this agreement is satisfactory, considering that Varghese and Hanson measurements were made at room temperature and very low pressure (approximately 25 mm), whereas the results of this study were extrapolated from high-temperature data taken at much higher pressures. The measurements of the half widths made with the stainless-steel cell are offset from the copper cell data for reasons not understood at this time, but each set of data shows approximately the same temperature dependence.

In both methods, uncertainty in the partial pressure of water vapor presents a problem, and it is difficult to choose which is the more accurate. Equation (4) gives a very good fit to the data for each line, indicating that this method would work well on extrapolating half widths to combustion temperatures.

In contrast to the broadening of CO attributable to nitrogen (Refs. 1 and 2), argon (Ref. 1), and carbon dioxide (Ref. 8) measured by others where the half width decreases with increasing rotational index, the half widths for water vapor broadening show very little dependence on rotational index.

Table 1. Summary of Experimental Water Vapor Broadened Half Widths

	P (2)	P (3)	P (7)
T_0 , K	300	300	300
$\gamma_{H_2O}^0(T_0)$, cm ⁻¹ -atm ⁻¹	0.08124 ± 0.00014	0.09725 ± 0.00015	0.10428 ± 0.00016
N_i	-0.73422 ± 0.00674	-0.70168 ± 0.00073	-0.76686 ± 0.00006
σ	0.00145	0.00172	0.00207
Number of Data Points	47	57	80

Table 2. Average Half Widths for Water Vapor Broadening of CO at Temperatures Studied

Temperature, K	P(2)		P(3)		P(7)	
	$\gamma_{H_2O}^0(T)$, cm ⁻¹ -atm ⁻¹	Data Point No.	$\gamma_{H_2O}^0(T)$, cm ⁻¹ -atm ⁻¹	Data Point No.	$\gamma_{H_2O}^0(T)$, cm ⁻¹ -atm ⁻¹	Data Point No.
400	0.06554 ± 0.00023	7	0.07991 ± 0.00056	12	0.08369 ± 0.00054	11
500	0.5638 ± 0.00033	7	0.06610 ± 0.00027	5	0.06941 ± 0.00085	6
600	0.04741 ± 0.00039	7	0.05974 ± 0.00027	10	0.06210 ± 0.00026	7
700	0.04494 ± 0.00028	7	0.05426 ± 0.00030	6	0.05461 ± 0.00046	16
800	0.03954 ± 0.00037	7	0.04968 ± 0.00019	7	0.04904 ± 0.00039	12
900	0.03701 ± 0.00049	5	0.04503 ± 0.00033	8	0.04541 ± 0.00017	13
1000	0.03293 ± 0.00017	7	0.04136 ± 0.00028	9	0.04109 ± 0.00027	15

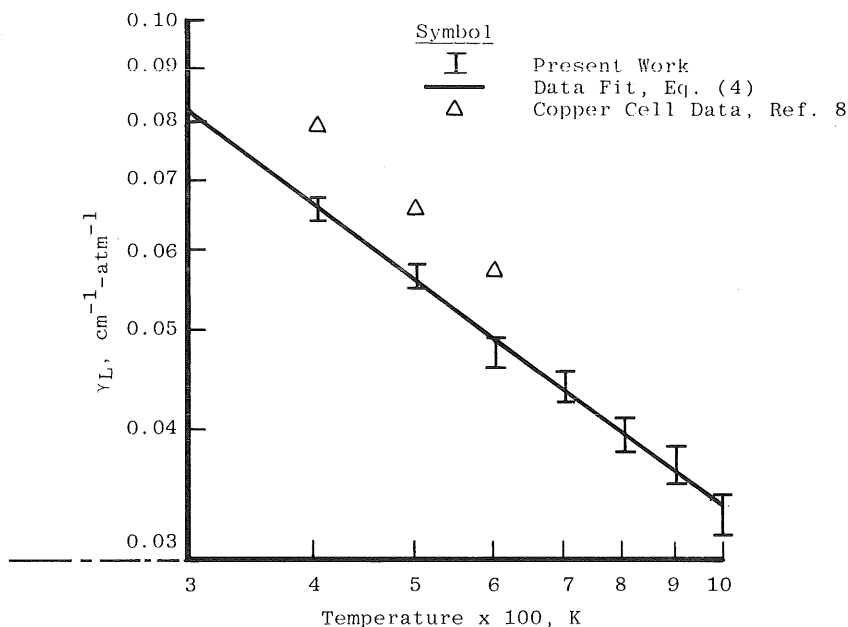
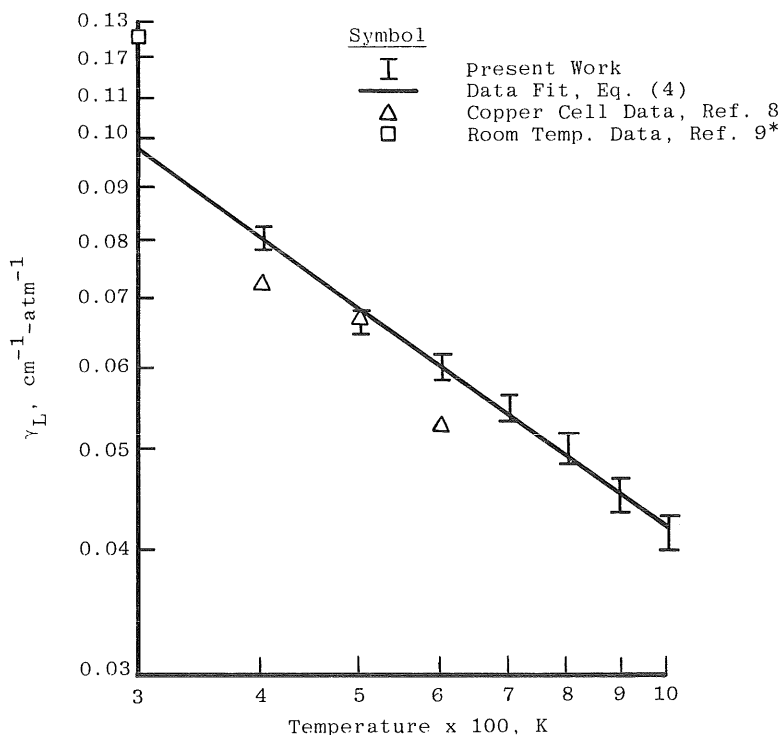


Figure 4. Temperature dependence of the experimental half widths for the P(2) CO line broadened by water vapor.



*For R(2) line, same half width as the P(3) line according to Anderson-Tsao-Curnutte theory.

Figure 5. Temperature dependence of the experimental half widths for the P(3) CO line broadened by water vapor.

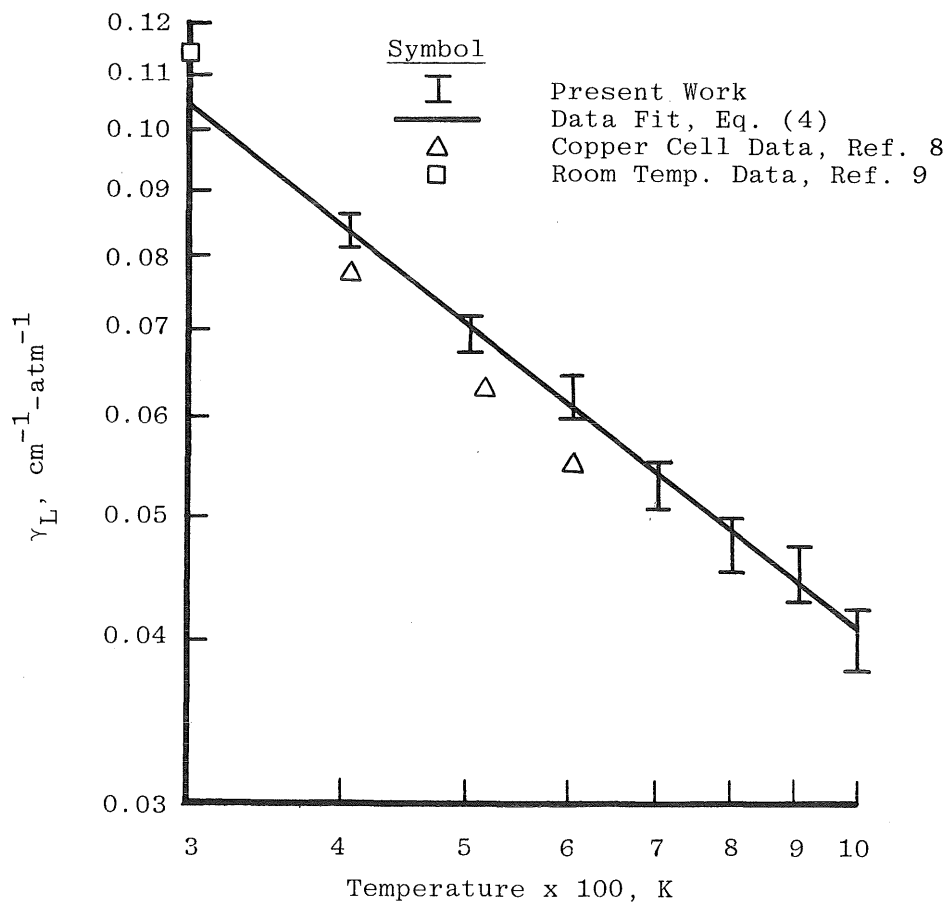


Figure 6. Temperature dependence of the experimental half widths for the P(7) CO line broadened by water vapor.

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